D4

PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : D21H 23/02 — A1

(11) International Publication Number: **WO 97/04171**

(43) International Publication Date: 6 February 1997 (06.02.97)

(21) International Application Number: PCT/US96/11780

(22) International Filing Date: 16 July 1996 (16.07.96)

(30) Priority Data:
08/505,838 21 July 1995 (21.07.95) US

(71) Applicant: KIMBERLY-CLARK CORPORATION [US/US]; 401 North Lake Street, Neenah, WI 54956 (US).

(72) Inventors: SCHROEDER, Wen, Zyo; 3120 West Capitol Drive, Appleton, WI 54914 (US). ANDERSON, Gary, Vance; 8298 Anderson Avenue, Larsen, WI 54947 (US). KRZYSIK, Duane, Gerard; 1112 East Melrose Place, Appleton, WI 54911 (US). SHANKLIN, Gary, Lee; 1308 South Clara Street, Appleton, WI 54915 (US). SMITH, Michael, John; 1124 Tullar Road, Neenah, WI 54956 (US).

(74) Agents: CROFT, Gregorgy, E. et al.; Kimberly-Clark Corporation, 401 North Lake Street, Neenah, WI 54956 (US).

(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: METHOD FOR MAKING SOFT TISSUE WITH IMPROVED BULK SOFTNESS AND SURFACE SOFTNESS

(57) Abstract

The invention relates to tissue products having improved softness properties and methods of making them. Specifically, improved softness is achieved by incorporating one or more softeners/debonders into the fiber furnish at the wet end of the tissue machine prior to formation, followed by a topical treatment with one or more softeners/debonders after the tissue web is dried. The result is a tissue product with added bulk and a smooth surface feel, both properties contributing to improved softness characteristics.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	**GB**	United Kingdom	**MW**	Malawi
AT	Austria	**GE**	Georgia	**MX**	Mexico
AU	Australia	**GN**	Guinea	**NE**	Niger
BB	Barbados	**GR**	Greece	**NL**	Netherlands
BE	Belgium	**HU**	Hungary	**NO**	Norway
BF	Burkina Faso	**IE**	Ireland	**NZ**	New Zealand
BG	Bulgaria	**IT**	Italy	**PL**	Poland
BJ	Benin	**JP**	Japan	**PT**	Portugal
BR	Brazil	**KE**	Kenya	**RO**	Romania
BY	Belarus	**KG**	Kyrgystan	**RU**	Russian Federation
CA	Canada	**KP**	Democratic People's Republic of Korea	**SD**	Sudan
CF	Central African Republic			**SE**	Sweden
CG	Congo	**KR**	Republic of Korea	**SG**	Singapore
CH	Switzerland	**KZ**	Kazakhstan	**SI**	Slovenia
CI	Côte d'Ivoire	**LI**	Liechtenstein	**SK**	Slovakia
CM	Cameroon	**LK**	Sri Lanka	**SN**	Senegal
CN	China	**LR**	Liberia	**SZ**	Swaziland
CS	Czechoslovakia	**LT**	Lithuania	**TD**	Chad
CZ	Czech Republic	**LU**	Luxembourg	**TG**	Togo
DE	Germany	**LV**	Latvia	**TJ**	Tajikistan
DK	Denmark	**MC**	Monaco	**TT**	Trinidad and Tobago
EE	Estonia	**MD**	Republic of Moldova	**UA**	Ukraine
ES	Spain	**MG**	Madagascar	**UG**	Uganda
FI	Finland	**ML**	Mali	**US**	United States of America
FR	France	**MN**	Mongolia	**UZ**	Uzbekistan
GA	Gabon	**MR**	Mauritania	**VN**	Viet Nam

METHOD FOR MAKING SOFT TISSUE WITH IMPROVED BULK SOFTNESS AND SURFACE SOFTNESS

Background of the Invention

Improving the softness of tissues is a continuing objective in tissue manufacture. In general, prior efforts have been directed at reducing the inter-fiber bonding within the tissue structure or coating the tissue surface with chemicals which improve the surface feel. Softness, however, is a perceived property of tissues comprising many factors including bulk softness and surface smoothness. To date, efforts have tended to focus on one or the other. Hence, there is a need for a method which improves both bulk softness and surface softness.

Summary of the Invention

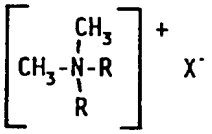
It has now been discovered that softness of tissues can be improved by the combined addition of one or more softener/debonders (hereinafter defined) to the tissue making furnish, followed by a second addition of one or more softener/debonders to the surface of the dried tissue. The initial introduction of the softener/debonder to the furnish provides more of a bulk softness to the tissue, while the subsequent topical application imparts a more smooth or slick surface feel. The combination results in a very soft-feeling tissue product.

More specifically, the invention resides in a method for making soft tissue comprising: (a) forming an aqueous suspension of papermaking fibers having from about 0.01 to about 6 weight percent based on dry fiber of one or more softener/debonders; (b) forming a tissue web by depositing the aqueous suspension of papermaking fibers onto a forming

fabric; (c) dewatering and drying the web; and (d) topically applying to the dried web from about 0.01 to about 10 weight percent, based on dry fiber, of one or more softener/debonders. The softener/debonder which is topically applied to the dry web can be the same softener/debonder added to the furnish prior to forming the tissue web, or it can be different.

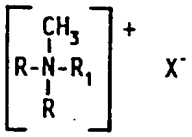
As used herein, "softener/debonder" is a chemical compound selected from the group consisting of quaternary ammonium compounds, quaternized protein compounds, phospholipids, silicone quaternaries, quaternized, hydrolyzed wheat protein/dimethicone phosphocopolyol copolymer, organoreactive polysiloxanes, and silicone glycols.

Suitable quaternary ammonium compounds have the following structures:



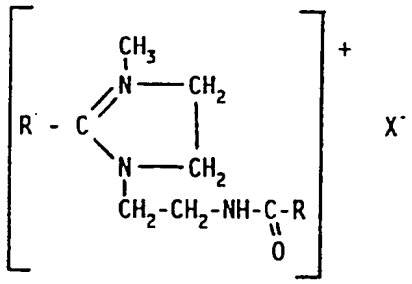
wherein X = chloride, methyl sulfate, or other compatible counterion; and
R = aliphatic, saturated or unsaturated C_8 - C_{22};

and



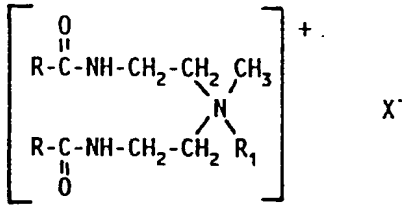
wherein X = chloride, methyl sulfate, or other compatible counterion;
R = aliphatic, saturated or unsaturated C_8 - C_{22}; and
R_1= benzyl or epoxy group;

and



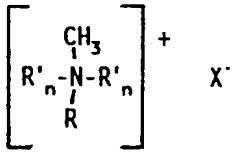
wherein X = chloride, methyl sulfate, or other compatible counterion; and
R = aliphatic, saturated or unsaturated C_8-C_{22};

and



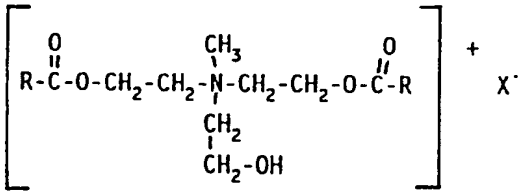
wherein X = methyl sulfate, chloride, or other compatible counterion;
R = aliphatic, normal, saturated or unsaturated, C_8 - C_{22}; and
R_1 = 2-hydroxyethyl or 2-hydroxypropyl;

and



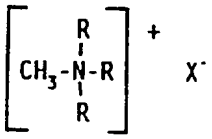
wherein R = aliphatic, normal or branched, saturated or unsaturated, C_8 - C_{22};
X = chloride, methyl sulfate, ethyl sulfate, or other compatible counterion;
R'= 2-hydroxyethyl or polyethoxyethanol; and
n = 1 to 50;

and



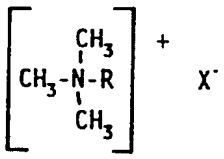
wherein R = C_8 - C_{22}; and
X = methyl sulfate, chloride, or other compatible counterion;

and



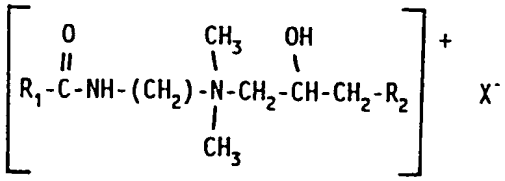
wherein R = aliphatic alkyl, normal or branched, saturated or unsaturated, C_8 - C_{22}; and
X = chloride, methyl sulfate or other compatible counterion.

and



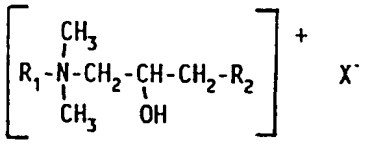
wherein R = aliphatic, saturated or unsaturated, C_8 - C_{22}; or allyl-; or R'-O-CH_2-CH_2-CH_2- where R'= normal or branched, C_4 - C_{18}; and
X = chloride, sulfate or any other compatible counterion.

Suitable quaternized protein compounds include the following structures:



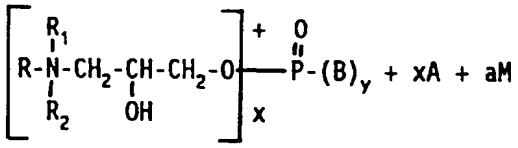
wherein R_1 = fatty acid radical, saturated or unsaturated, C_{12} - C_{22};
R_2 = hydrolyzed soy protein, hydrolyzed silk protein, collagen, keratin moiety or hydrolyzed wheat protein; and
X = chloride, lactate or other compatible counterion;

and



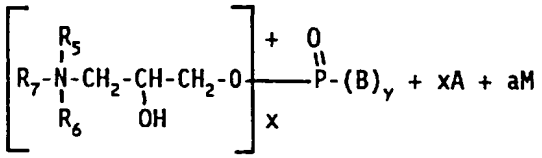
wherein R_1 = fatty acid radical, saturated or unsaturated, C_{12} - C_{22};
R_2 = hydrolyzed collagen or keratin moiety; and
X = chloride, lactate or other compatible counterion.

Suitable phospholipids include, without limitation, those having the following structures:

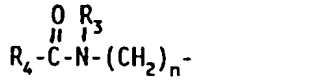


wherein x = 1 to 3;
x + y = 3;
a = 0 to 2;
B = O^- or OM;
A = an anion;
M = a cation; and
R, R_1 & R_2 can be the same or different, are alkyl, substituted alkyl, alkyl aryl or alkenyl groups of up to 16 carbon atoms and the total carbon atoms of R + R_1 + R_2 = 10 to 24;

and

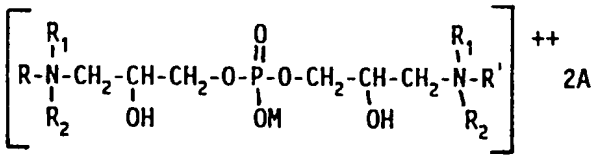


wherein x = 1 to 3;
x + y = 3;
a = 0 to 2;
B = O⁻ or OM;
A = an anion;
M = a cation;
R_5, R_6 may be the same or different, are alkyl, hydroxyalkyl, carboxyalkyl of up to C_6, or polyoxyalkylene of up to C_{10}; or R_5, R_6 and the nitrogen they are attached to may represent an N-heterocycle; and
R_7 = an amidoamine moiety of the formula:

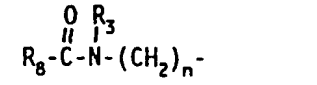


wherein n = 2 to 6;
R_3 = hydrogen or alkyl, hydroxyalkyl or alkenyl of up to 6 carbons; or cycloalkyl of up to 6 carbon atoms, or polyoxyalkylene of up to 10 carbon atoms; and
R_4 = alkyl, alkenyl, alkoxy or hydroxyalkyl, C_5-C_{21}, or aryl or alkaryl of up to C_{20};

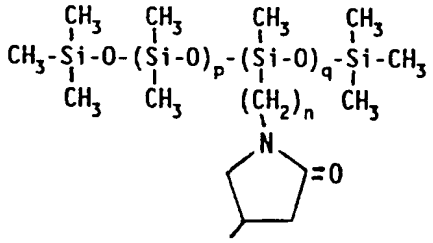
and



wherein A = an anion;
M = a cation;
R, R_1 & R_2 can be the same or different, are alkyl, substituted alkyl, alkyl aryl or altkenyl groups of up to 16 carbon atoms, and the total carbon atoms of R + R_1 + R_2 = 10 to 24; and
R' is an amidoamine moiety of the structure:

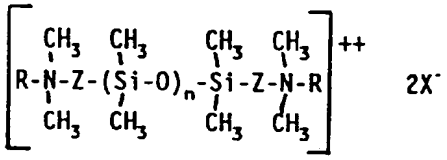


wherein n = 2 to 6;
R_3 = hydrogen or alkyl, hydroxyalkyl or alkenyl of up to 6 carbons; or cycloalkyl of up to 6 carbon atoms, or polyoxyalkylene of up to 10 carbon atoms; and
R_8 has the following structure:



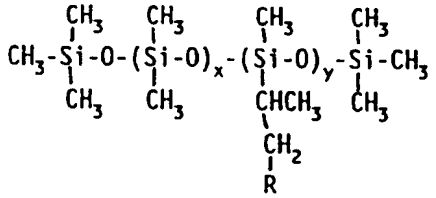
wherein n = 3 or greater;
p = 1 to 1000;
q = 1 to 25.

Suitable silicone quaternaries include the following structure:

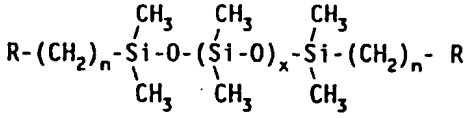


wherein R = alkyl group, C_{12} - C_{18};
Z = $-CH_2-CH_2-CH_2-O-(CH_2)_3-$;
X = alkoxy, chloride or other compatible counterion; and
n = 1 to 50.

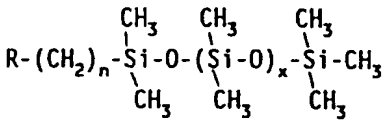
Suitable organoreactive polysiloxanes include the following structures:



and

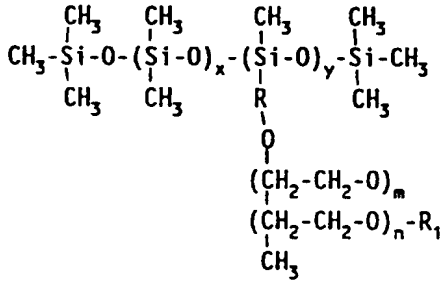


and



wherein R = amine, carboxy, hydroxy, or epoxy;
n = 3 or greater;
x = 1 to 1000; and
y = 1 to 25.

Suitable silicone glycols include the following structure:



wherein R = alkyl group, C_1 - C_6;
R_1 = acetate or hydroxy group;
x = 1 to 1000;
y = 1 to 50;
m = 1 to 30; and
n = 1 to 30.

When a combination of softener/debonder is desired, the combination can be added to the thick stock simultaneously or separately. The combinations can contain one or more compounds from the above groups and added to the slurry, either in a premixed form or individually metered.

The final tissue sheet comprises from about 0.01 to about 6 percent (by weight of the fiber) of the softener/debonders added to the wet end of the tissue making process, individually or in combination. More preferably, the final tissue sheet comprises from about 0.1 to about 3 percent of the softener/debonder added at the wet end, based on the weight of the fiber.

Softener/debonders used for the topical treatment can be delivered in an aqueous solution or be dissolved in a suitable solvent such as propylene glycol, ethylene glycol, polyethylene glycol, isopropyl alcohol, methanol, ethanol or other organic solvents. They can be applied to the surface of the basesheet individually or in combination with others. It is preferred that the composition for topical treatment comprises from about 1 to about 100 weight percent of the softener/debonder (individually or in combination), more preferably from about 35 to about 80 weight percent. It is also preferred that the softener/debonder be topically added to the tissue sheet at an add-on ratio of from about 0.01 to about 10 weight percent of the fiber, and more preferably from about 0.1 to about 2 weight percent of the fiber.

Suitable methods for the topical treatment include, but are not limited to spraying, rotogravure printing, trailing blade coating, flexographic printing, and the like.

Examples

Example 1

A 2-ply, wet-pressed, creped tissue was made using a layered headbox. The first stock layer (the layer which ultimately contacts the Yankee dryer surface) contained eucalyptus hardwood fiber and provided 60 dry weight percent of the tissue sheet. The remaining 40 percent of the tissue sheet was provided via a second stock layer consisting of northern softwood kraft pulp. The total basis weight of the sheet was 7.3 pounds per 2880 square feet of air dried tissue. Two strength agents were added to the fiber stock layers prior to the headbox. Parez 631NC (a glyoxalated polyacrylamide from Cytec Industries, Inc.) was metered into the softwood thick stock at 0.08 to 0.1 percent of the total fiber

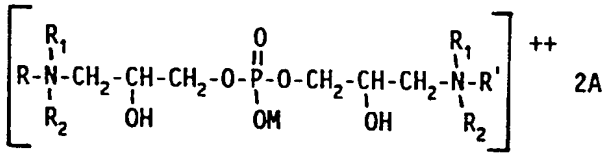
weight. Another strength agent, Kymene 557 LX (commercially available from Hercules, Inc.) was metered into both the hardwood and the softwood thick stock at 0.05 and 0.1 percent of the total fiber weight, respectively.

A quaternary ammonium compound softener/debonder (methyl-1-oleyl amidoethyl-2-oleyl imidazolinium methyl sulfate identified as Varisoft 3690 available from Witco Corporation, 90 percent active matter) was added to the hardwood thick stock at 0.17 percent of the total fiber weight.

After drying and creping, the tissue sheet was plied together with a like sheet to form a two-ply tissue. The hardwood layer of both plies was rotogravure-printed with a 40 percent emulsion of an organoreactive polysiloxane (FTS-226 made by OSi Specialties, Inc.) at an add-on amount of 1 percent per ply based on the weight of fiber. The resulting tissue product had increased bulk with improved surface smoothness.

Example 2

A 2-ply layered tissue was made as described in Example 1, except instead of rotogravure-printing both plies with an organoreactive polysiloxane, both plies were instead coated with a silicone phospholipid (Mona Industries, Inc., Item Code #54146, Lot 2426, 25-30% active) having the following structure:



2A

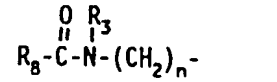
wherein A = chloride ion;

M = sodium ion;

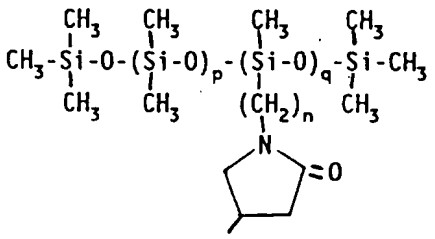
$R_1 = R_2 = -CH_3$

R can be alkyl, substituted alkyl, alkyl aryl or altkenyl groups of up to 16 carbon atoms, and the total carbon atoms of $R + R_1 + R_2 = 10$ to 24; and

R' is an amidoamine moiety of the structure:



wherein n = 3;
R_3 = hydrogen; and
R_8 has the following structure:

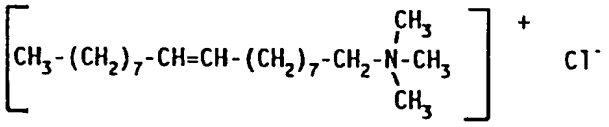


wherein n = 3;
p = 90;
q = 1.

A trailing blade coater was used to apply the silicone phospholipid. The blade angle was set at 30° and blade pressures were varied between 20 and 40 psi to deliver different levels of addition. The resulting tissue products had increased bulk and smooth surface feel.

Example 3

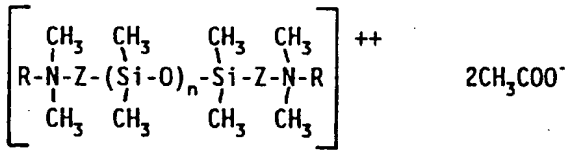
A 2-ply tissue was made as described in Example 2, except both plies were coated with a quaternary ammonium compound (olealkonium chloride, Mackernium KP made by McIntyre Group, LTD., 50% active) having the following structure:



The resulting tissue products had increased bulk and smooth surface feel.

Example 4

A 2-ply layered tissue was made as described in Example 2, except both plies were coated with a silicone quaternary compound (Abilquat 3272 made by Goldschmidt Chemical Corporation, 50% active) having the following structure:



wherein R = alkyl group, C_{12} - C_{18};
Z = $-CH_2-CH_2-CH_2-O-(CH_2)_3-$; and
n = 1 to 50.

The resulting tissue products had increased bulk and smooth surface feel.

Example 5

A 2-ply layered basesheet was made as described in Example 2, except both plies were printed with an aqueous composition comprising 50% of organopolydimethylsiloxane (FTS-226) and 50% quaternary ammonium compound (Mackernium KP). The resulting tissue products had increased bulk and smooth surface feel.

Example 6

A 2-ply layered basesheet was made as described in Example 1, except both plies were coated with an aqueous composition comprising 40% quaternary ammonium compound (Mackernium NLE made by McIntyre Group, LTD.), 40% organopolydimethylsiloxane (FTS-226) and 20% water. Mackernium NLE is an alkylamidopropyl epoxypropyl diammonium chloride, 100 percent active.

The resulting tissue products had increased bulk and smooth surface feel.

Example 7

A two-ply layered basesheet was made as described in Example 2, except both plies were coated with an aqueous composition comprising 25% quaternary ammonium compound (Mackernium KP), 25% organopolysiloxane (FTS-226) and 50% propylene glycol. The resulting tissue products had increased bulk and smooth surface feel.

Example 8

A one-ply, uncreped, through-air-dried tissue was made using a layered headbox. The two outer layers contained bleached eucalyptus

hardwood kraft pulp processed through a Maule shaft disperser with a power input of 80 kilowatts at a consistency of about 34 percent and at a temperature of 184°F. The two outer layers made up 70 percent of the tissue sheet by weight of fiber. The middle layer constituted the remaining 30 percent of the tissue web and consisted of bleached northern softwood kraft pulp. The total basis weight of the sheet was 33.9 grams per square meter of air-dried tissue. The inner layer was refined to obtain sufficient dry strength in the final product. A wet strength agent (Parez 631NC) was metered into the inner layer at a rate of 5 kilograms per tonne or 0.5 percent of the weight of fiber. A softener/debonder (quaternary imidazolinium, fatty acid alkoxylate and polyether with 200 - 800 molecular weight, identified as DPSC 5299-8 from Witco Corporation) was added to the two outer layers at a rate of 5.25 kilograms per tonne (0.525 percent) of the total fiber weight. The thick stock of all layers was diluted to approximately 0.12 percent consistency prior to forming, dewatering and drying the tissue web.

After drying, the tissue was coated with a silicone diquaternary compound (Abilquat 3272) similar to Example 4. The resulting tissue product had a smoother surface feel compared to the tissue without coating.

It will be appreciated that the foregoing examples, given for purposes of illustration, are not to be construed as limiting the scope of this invention, which is defined by the following claims and all equivalents thereto.

We Claim:

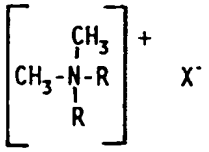
1. A method for making a soft tissue comprising:
(a) forming an aqueous suspension of papermaking fibers having from about 0.01 to about 6 weight percent, based on dry fiber, of one or more softener/debonders;
(b) forming a tissue web by depositing the aqueous suspension of papermaking fibers onto a forming fabric;
(c) dewatering and drying the tissue web; and
(d) topically applying to the dry tissue web from about 0.01 to about 10 weight percent, based on dry fiber, of one or more softener/debonders.

2. The method of Claim 1 wherein the softener/debonder is selected from the group consisting of quaternary ammonium compounds, quaternized protein compounds, phospholipids, silicone quaternaries, organoreactive polysiloxanes and silicone glycols.

3. The method of Claim 1 wherein the amount of softener/debonder added to the fiber suspension is from about 0.1 to about 3 dry weight percent based on the amount of fiber.

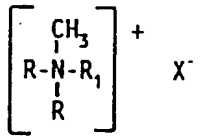
4. The method of Claim 1 wherein the amount of softener/debonder topically applied to the dried web is from about 0.1 to about 10 dry weight percent, based on the amount of fiber.

5. The method of Claim 1 wherein at least one of the softener/debonders is a quaternary ammonium compound having the following structure:



wherein X = chloride, methyl sulfate, or other compatible counterion; and
R = aliphatic, saturated or unsaturated C_8 - C_{22}.

6. The method of Claim 1 wherein at least one of the softener/debonders is a quaternary ammonium compound having the following structure:

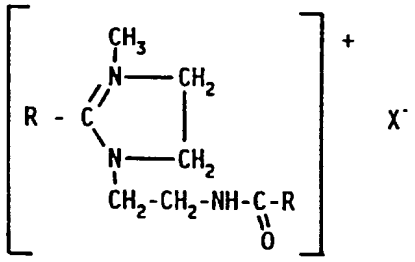


wherein X = chloride, methyl sulfate, or other compatible counterion;

R = aliphatic, saturated or unsaturated C_8 - C_{22}; and

R_1= benzyl or epoxy group.

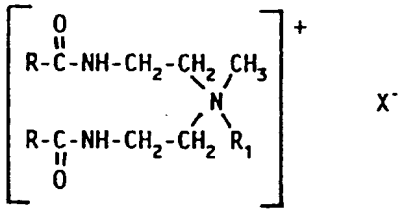
7. The method of Claim 1 wherein at least one of the softener/debonders is a quaternary ammonium compound having the following structure:



wherein X = chloride, methyl sulfate, or other compatible counterion; and

R = aliphatic, saturated or unsaturated C_8-C_{22}.

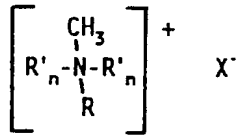
8. The tissue of Claim 1 wherein at least one of the softener/debonders is a quaternary ammonium compound having the following structure:



wherein X = methyl sulfate, chloride, or other compatible counterion;

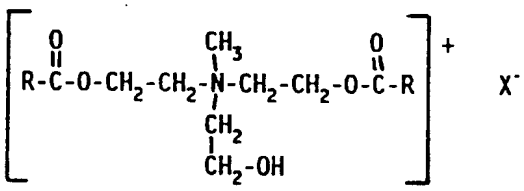
R = aliphatic, normal, saturated or unsaturated, C_8 - C_{22};
R_1 = 2-hydroxyethyl or 2-hydroxypropyl;

9. The tissue of Claim 1 wherein at least one of the softener/debonders is a quaternary ammonium compound having the following structure:



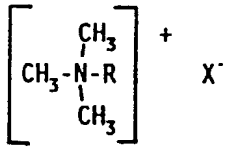
wherein R = aliphatic, normal or branched, saturated or unsaturated, C_8 - C_{22};
X = chloride, methyl sulfate, ethyl sulfate, or other compatible counterion;
R'= 2-hydroxyethyl or polyethoxyethanol; and
n = 1 to 50.

10. The tissue of Claim 1 wherein at least one of the softener/debonders is a quaternary ammonium compound having the following structure:



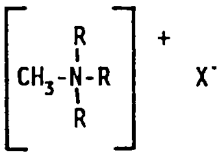
wherein R = C_8 - C_{22}; and
X = methyl sulfate, chloride, or other compatible counterion.

11. The tissue of Claim 1 wherein at least one of the softener/debonders is a quaternary ammonium compound having the following structure:



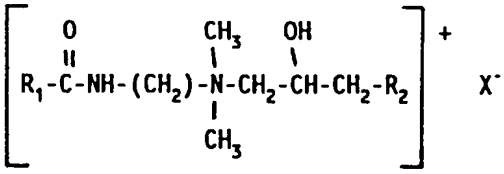
wherein R = aliphatic, saturated or unsaturated, C_8 - C_{22}; or allyl-; or R'-O-CH_2-CH_2-CH_2- where R'= normal or branched, C_4 - C_{18}; and
X = chloride, sulfate or any other compatible counterion.

12. The tissue of Claim 1 wherein at least one of the softener/debonders is a quaternary ammonium compound having the following structure:



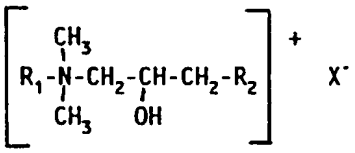
wherein R = aliphatic alkyl, normal or branched, saturated or unsaturated, C_8 - C_{22}; and
X = chloride, methyl sulfate, or other compatible counterion.

13. The method of Claim 1 wherein at least one of the softener/debonders is a quaternized protein compound having the following structure:



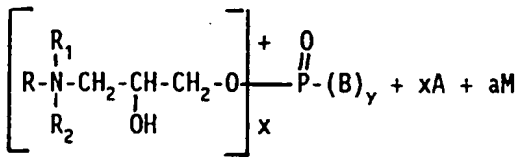
wherein R_1 = fatty acid radical, saturated or unsaturated, C_{12} - C_{22};
R_2 = hydrolyzed soy protein, hydrolyzed silk protein, hydrolyzed wheat protein, collagen moiety, or keratin moiety; and
X = chloride, lactate, or other compatible counterion.

14. The method of Claim 1 wherein at least on of the softener/debonders is a quaternized protein compound having the following structure:



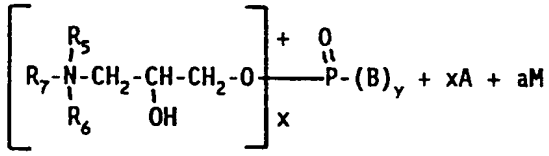
wherein R_1 = fatty acid radical, saturated or unsaturated, C_{12} - C_{22};
R_2 = hydrolyzed collagen or keratin moiety; and
X = chloride, lactate, or other compatible counterion.

15. The tissue of Claim 1 wherein at least one of the softener/debonders is a phospholipid having the following structure:

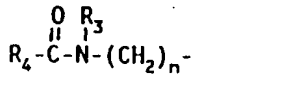


wherein x = 1 to 3;
x + y = 3;
a = 0 to 2;
B = O^- or OM;
A = an anion;
M = a cation; and
R, R_1 & R_2 can be the same or different, are alkyl, substituted alkyl, alkyl aryl or alkenyl groups of up to 16 carbon atoms and the total carbon atoms of R + R_1 + R_2 = 10 to 24.

16. The tissue of Claim 1 wherein at least one of the softener/debonders is a phospholipid having the following structure:



wherein x = 1 to 3;
x + y = 3;
a = 0 to 2;
B = O^- or OM;
A = an anion;
M = a cation;
R_5, R_6 may be the same or different, are alkyl, hydroxyalkyl, carboxyalkyl of up to C_6, or polyoxyalkylene of up to C_{10}; or R_5, R_6 and the nitrogen they are attached to may represent an N- heterocycle; and
R_7 = an amidoamine moiety of the formula:

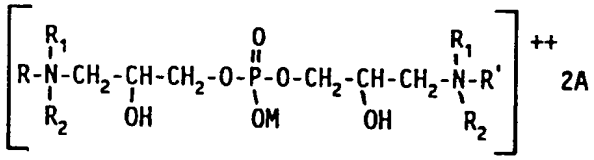


wherein n = 2 to 6;

R_3 = hydrogen or alkyl, hydroxyalkyl or alkenyl of up to 6 carbons; or cycloalkyl of up to 6 carbon atoms, or polyoxyalkylene of up to 10 carbon atoms; and

R_4 = alkyl, alkenyl, alkoxy or hydroxyalkyl, C_5 - C_{21}, or aryl or alkaryl of up to C_{20}.

17. The tissue of Claim 1 wherein at least one of the softener/debonders is a phospholipid having the following structure:

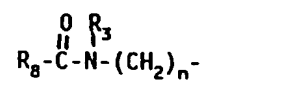


wherein A = an anion;

M = a cation;

R, R_1 & R_2 can be the same or different, are alkyl, substituted alkyl, alkyl aryl or altkenyl groups of up to 16 carbon atoms, and the total carbon atoms of R + R_1 + R_2 = 10 to 24; and

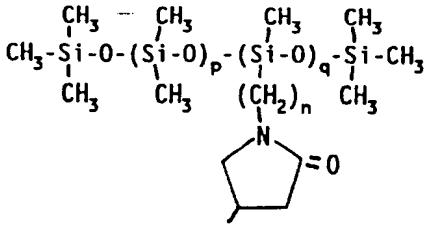
R' is an amidoamine moiety of the structure:



wherein n = 2 to 6;

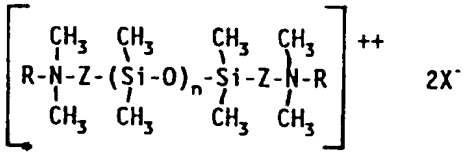
R_3 = hydrogen or alkyl, hydroxyalkyl or alkenyl of up to 6 carbons; or cycloalkyl of up to 6 carbon atoms, or polyoxyalkylene of up to 10 carbon atoms; and

R_8 has the following structure:



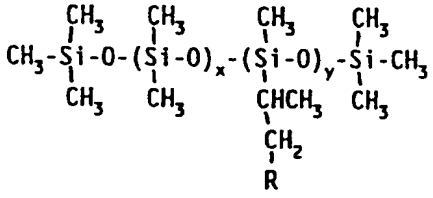
wherein n = 3 or greater;
p = 1 to 1000; and
q = 1 to 25.

18. The method of Claim 1 wherein at least one of the softener/debonders is a silicone quaternary having the following structure:



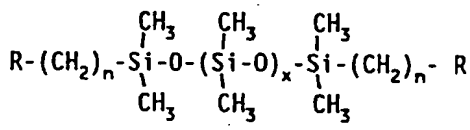
wherein R = alkyl group, C_{12} - C_{18};
Z = $-CH_2-CH_2-CH_2-O-(CH_2)_3-$;
X = alkoxy, chloride or other compatible counterion; and
n = 1 to 50.

19. The method of Claim 1 wherein at least one of the softener/debonders is a organoreactive polysiloxane having the following structure:



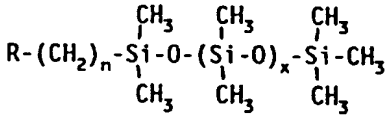
wherein R = amine, carboxy, hydroxy, or epoxy;
n = 3 or greater;
x = 1 to 1000; and
y = 1 to 25.

20. The method of Claim 1 wherein at least one of the softener/debonders is an organoreactive polysiloxane having the following structure:



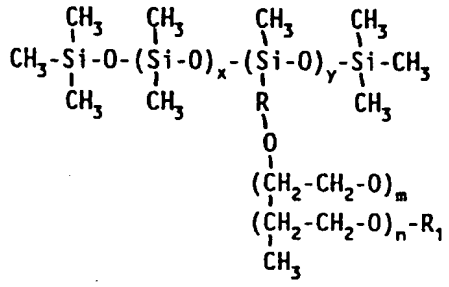
wherein R = amine, carboxy, hydroxy, or epoxy;
n = 3 or greater;
x = 1 to 1000; and
y = 1 to 25.

21. The method of Claim 1 wherein at least one of the softener/debonders is an organoreactive polysiloxane having the following structure:



wherein R = amine, carboxy, hydroxy, or epoxy;
n = 3 or greater;
x = 1 to 1000; and
y = 1 to 25.

22. The method of Claim 1 wherein at least one of the softener/debonders is a silicone glycol having the following formula:



wherein R = alkyl group, C_1 - C_6;
R_1 = acetate or hydroxyl group;
x = 1 to 1000;
y = 1 to 50;

m = 1 to 30; and
n = 1 to 30.

23. The method of Claim 1 wherein at least one of the softeners/debonders is a quaternized, hydrolyzed wheat protein/dimethicone phosphocopolyol copolymer.

24. The method of Claim 1 wherein the softener/debonder added to the dried web is carried by a solvent selected from the group consisting of water, propylene glycol, ethylene glycol, polyethylene glycol, isopropyl alcohol, methanol and ethanol.

INTERNATIONAL SEARCH REPORT

Inter nal Application No
PCT/US 96/11780

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 D21H23/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 D21H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,4 447 294 (OSBORN III THOMAS W) 8 May 1984 see claims 1,3; example II ---	1,2,5-12
A	EP,A,0 347 153 (PROCTER & GAMBLE) 20 December 1989 see claims 1-3; example 1 ---	1,2, 19-21
A	US,A,3 755 220 (FREIMARK B ET AL) 28 August 1973 see column 2, line 48 - column 3, line 13 ---	1-3,5-12
A	US,A,4 158 594 (BECKER HENRY E ET AL) 19 June 1979 see column 6, line 45 - line 50 ---	1
	-/--	

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
18 October 1996	- 4. 12. 96

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (- 31-70) 340-2040, Tx. 31 651 epo nl, Fax: (- 31-70) 340-3016	Naeslund, P

Form PCT/ISA 210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Inte. ɔnal Application No
PCT/US 96/11780

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO,A,94 05857 (PROCTER & GAMBLE) 17 March 1994 see page 16, line 11 - page 19, line 12; figure 1 ---	1-4, 18-21,24
A	PATENT ABSTRACTS OF JAPAN vol. 013, no. 308 (C-617), 14 July 1989 & JP,A,01 093506 (YUJI KATO;OTHERS: 01), 12 April 1989, see abstract ---	1,2,18, 24
A	FR,A,2 481 333 (BEIERSDORF AG) 30 October 1981 -----	

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte onal Application No
PCT/US 96/11780

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US-A-4447294	08-05-84	NONE		
EP-A-0347153	20-12-89	AT-T-	120820	15-04-95
		AT-T-	132556	15-01-96
		AT-T-	122424	15-05-95
		AU-B-	634963	11-03-93
		AU-A-	3636389	21-12-89
		AU-B-	613765	08-08-91
		AU-A-	3636489	21-12-89
		AU-B-	634964	11-03-93
		AU-A-	3636889	21-12-89
		CA-A-	1328335	12-04-94
		CA-A-	1330382	28-06-94
		CA-A-	1328035	29-03-94
		DE-D-	68914338	11-05-94
		DE-T-	68914338	18-08-94
		DE-D-	68922024	11-05-95
		DE-T-	68922024	28-09-95
		DE-D-	68922529	14-06-95
		DE-T-	68922529	21-09-95
		DE-D-	68925309	15-02-96
		DE-T-	68925309	23-05-96
		EP-A-	0347154	20-12-89
		EP-A-	0347176	20-12-89
		EP-A-	0347177	20-12-89
		ES-T-	2070174	01-06-95
		ES-T-	2081303	01-03-96
		ES-T-	2050802	01-06-94
		ES-T-	2071658	01-07-95
		JP-A-	2224626	06-09-90
		JP-A-	2099690	11-04-90
		JP-A-	2099691	11-04-90
		US-A-	5059282	22-10-91
		AU-B-	634712	04-03-93
		AU-A-	3636589	26-07-90
		CA-A-	1330381	28-06-94
		JP-A-	3000900	07-01-91
		US-A-	5164046	17-11-92
US-A-3755220	28-08-73	CA-A-	978310	25-11-75

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. .onal Application No
PCT/US 96/11780

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US-A-4158594	19-06-79	BE-A-	765625	13-10-71
		CA-A-	978465	25-11-75
		DE-A-	2117806	28-10-71
		GB-A-	1294794	01-11-72
		US-A-	4208459	17-06-80
WO-A-9405857	17-03-94	US-A-	5246545	21-09-93
		US-A-	5246546	21-09-93
		AU-B-	666409	08-02-96
		AU-A-	5084193	29-03-94
		CA-A-	2143340	17-03-94
		CZ-A-	9500507	15-11-95
		EP-A-	0656971	14-06-95
		FI-A-	950863	19-04-95
		HU-A-	72350	29-04-96
		JP-T-	8500860	30-01-96
		NO-A-	950699	26-04-95
FR-A-2481333	30-10-81	DE-A-	3015733	29-10-81
		CA-A-	1195562	22-10-85
		JP-B-	3029920	25-04-91
		JP-A-	56159398	08-12-81
		SE-B-	446465	15-09-86
		SE-A-	8101912	25-10-81